UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Pyridine hydrodenitrogenation over an industrial NiMo/γ-Al_2O_3 catalyst

Application of gas phase models to liquid phase reactions

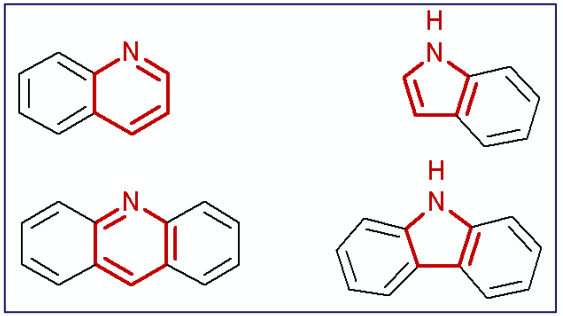
Chetan S. Raghuveer[a,b], Ruben De Bruycker[a], Joris W. Thybaut[a] , Leslie W Bolton[b] and Guy B. Marin[a]

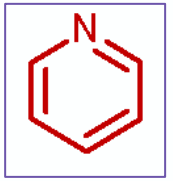
[a] Laboratory for Chemical Technology, Ghent University, Belgium
[b] BP plc, Sunbury, UK

Molecular Aspects of Catalysis by Sulfides , Satillieu, France 2013, May 12-16

ERIC

introduction and motivation





Environmental Issues
Government Regulations
Technical

Industrial reactors
- Three Phase reactions
- Kinetics may be disguised by hydrodynamic phenomenon

HDN

Trickle Bed Reactor
(Ni/Co)Mo/ Al_2O_3
200 – 400 ^{0}C
10 – 40 bar

Laboratory Reactors
- G-S / G-S-L reactions
- Intrinsic kinetics
- Used for model construction and discrimination

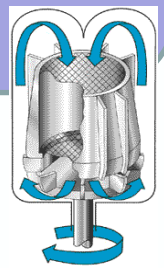
✓ Three phase
- ✓ Fischer Tropsch
- ✓ Hydrocracking
- ✓ Hydroprocessing

Bridging the gap between laboratory and industrial reactors

methodology

Extended set of gas phase experimentation

- Operating conditions
- Reaction pathway
- Detailed kinetics
- Model construction
- Evaluation estimated parameters

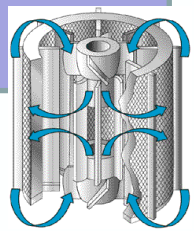


Berty Reactor

Limited liquid phase experimentation

–Effect of

- Liquid phase conditions on
- Formation of new compounds
- Solvent adsorption
- Assessment of liquid phase non ideality



Robinson Mahoney Reactor

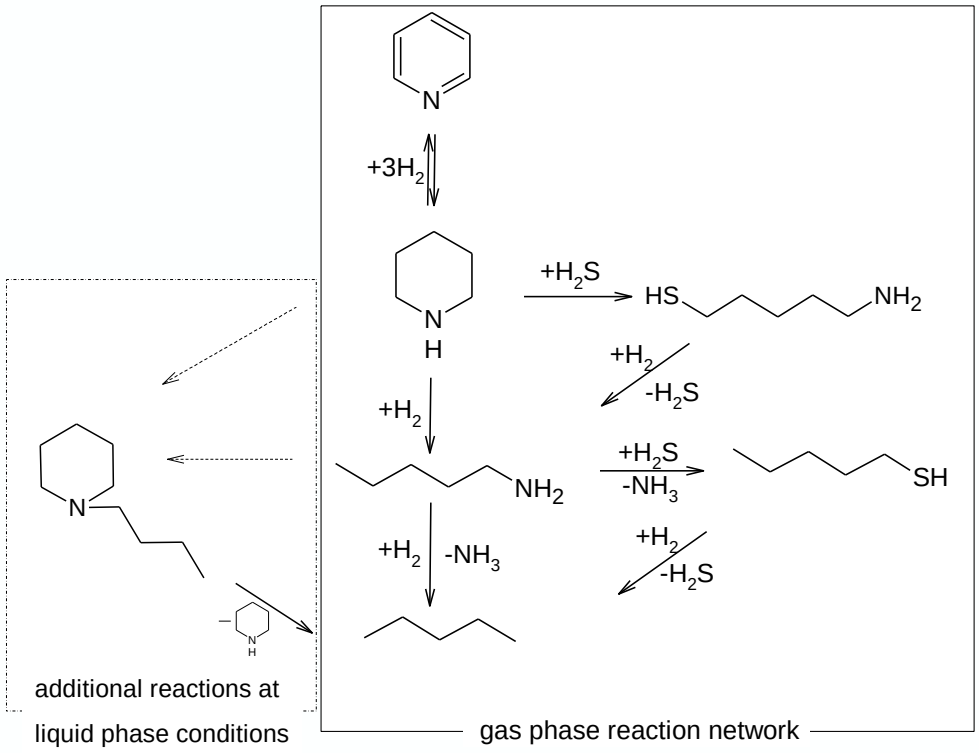
Three phase industrial reactor simulation

- Validation of data available from industrial / Pilot plant studies

outline

- Gas versus liquid phase experiments
  - network elucidation and difference in experimental programmes
- Liquid phase experimental results
- Thermodynamic non ideality in liquid phase
- Gas phase model and subsequent extension
- Liquid phase model
- Conclusions

gas and liquid phase experiments



- ✓ 1-pentylpiperidine observed in the liquid phase experiments only
  - ✓ observed with 2D GC - MS analysis
  - ✓ due to the varying operating conditions and higher bimolecular reactions
- ✓ Highly reactive/unstable intermediates not observed during analysis

- ✓ Challenges in extension
  - ✓ Differing denitrogenation kinetics in gas and liquid phase
  - ✓ Accounting for additional response in the model

comparison gas and liquid phase

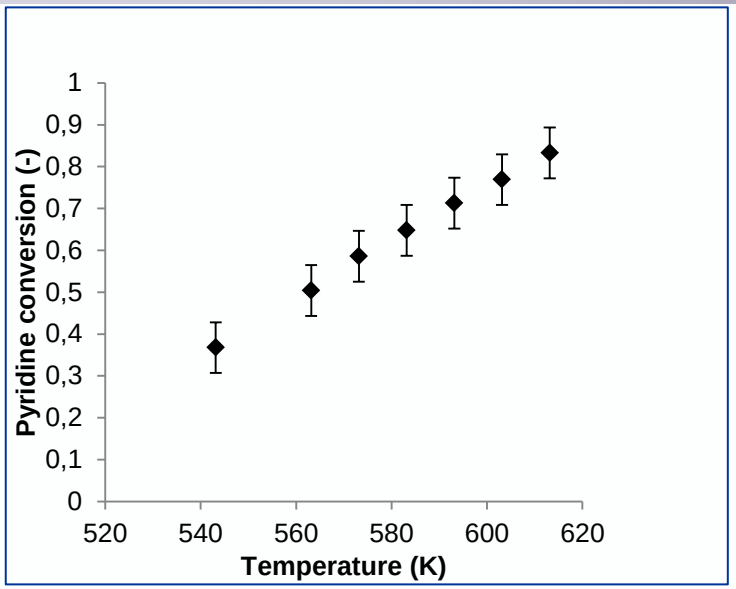
Program	Gas Phase[a]	Liquid Phase[b]
Reactor type	Berty type (CSTR)	Robinson Mahoney (CSTR)
Temperature range (K)	573 – 633	543 – 613
Pressure (MPa)	1.5 – 4.0	6.0 – 8.0
H_2/pyridine (mol/mol)	80 – 600	10 – 15
Space time (kg_{cat}.s/mmol)	0.36 – 1.8	0.65 – 3
Solvent/pyridine (mol/mol)	40	20 - 40
Solvent	n-hexane	Halpasol©

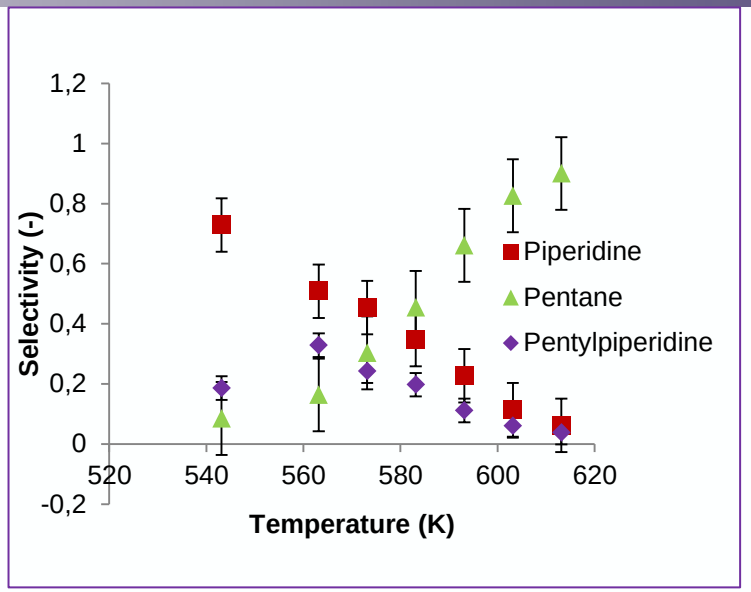
- ✓ Halpasol© : Mixture of C9-C14 paraffins

- ✓ Catalyst
  - ✓ $NiMoP/Al_2O_3$
  - ✓ Gas and liquid phase experiments
  - ✓ PROCATALYSE
- ✓ Literature insights
  - ✓ Temperature dependent
  - ✓ H_2S has a promoting effect on the C-N bond scission reaction

[a] R. Pille, G. Froment, Hydrotreatment and Hydrocracking of Oil Fractions 106 (1997) 403-413.
[B] This work
© : Haltermann products Gmbh

Liquid Phase Experimental results



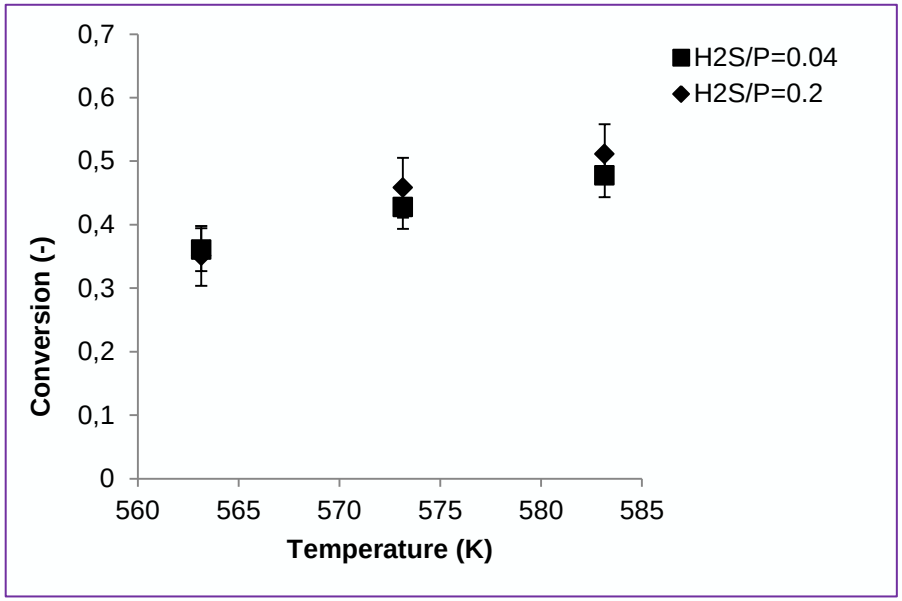


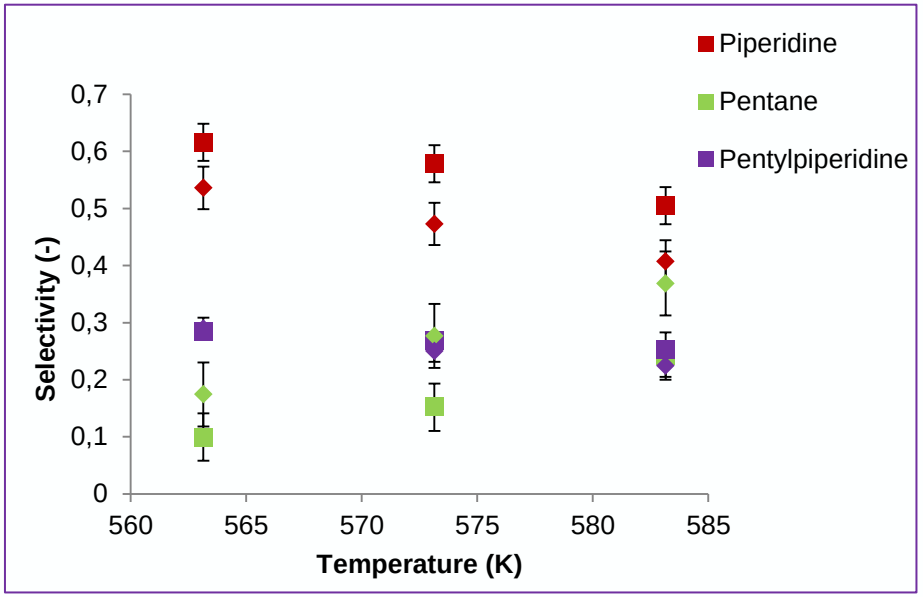
Operating conditions : 6.0 MPa, Spacetime : 790 kg_{cat}.s/mol H_2/pyridine : 10 (mol/mol) H_2S/pyridine : 0.04 (mol/mol)

✓ Assessment of Influence of temperature on HDN conversion ??

T	P	W/Fp°	H_2S/P	X	Selectivity		
					C5	PP	Pentyl PP
(K)	(MPa)	(kg.s/mol)	(-)	(-)	(-)	(-)	(-)
573	6.0	1129	0.04	0.64	0.34	0.44	0.22
583	6.0	790	0.04	0.65	0.45	0.35	0.20

Liquid Phase Experimental results



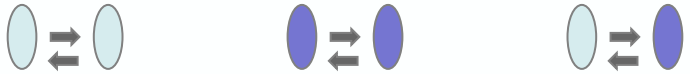


operating conditions : 6.0 MPa, spacetime : 439 kg_{cat}.s/mol, H_2/pyridine : 10 (mol/mol)

- ✓ H_2S has positive effect on the C-N bond scission
  - ✓ Higher hydrocarbon yield at higher H_2S/pyridine
  - ✓ Lower intermediate piperidine yield
- ✓ Substitution pathway is more pronounced at higher H_2S partial pressures

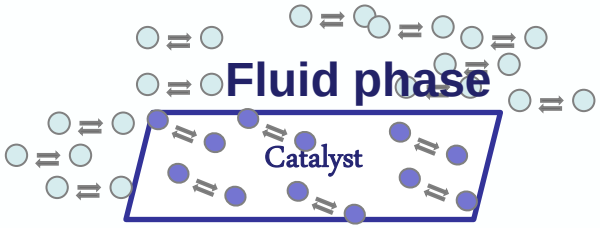
Thermodynamic non-ideality and effect of aggregation state

- ✓ Non ideality in liquid phase



$$f_i^v = f_i^l \qquad i = 1, \dots, n$$

- ✓ Effect of aggregation state (gas / liquid phase)
  - ✓ Description of kinetics, independent of phase in which reaction occurs
  - ✓ Difference between vapour and liquid phase kinetics is situated in the chemisorption step



$$A + * \leftrightarrow A - * \qquad K_{A,\tau} = \frac{\theta_{A-*}}{f_A \theta_*}$$

$$f_i = \varphi_i . P y_i = \varphi_k C_i V_m P \qquad \varphi_i = \frac{f_{i,G}}{P y_i}$$

gas phase model

- ✓ Development of gas phase model
  - ✓ Model assumptions based on previous literature insights[a]
  - ✓ Two site model related to CUS[b] and SA[b] sites
  - ✓ Model discrimination performed between 48 rival models
  - ✓ RDS : 3rd hydrogen addition and ring opening

$$R_{P\rightarrow PP} = k_{p,+} K_{P-PH2}\, K_{H2}\, K_P\, C_*{}^2 \sqrt{\delta\, \mu} \left(P_{H_2} P_{C_5H_5N} - \frac{1}{K_{Equi}} \frac{P_{C_5H_{10}NH}}{P_{H2}{}^2} \right)$$

$$R_{PP\rightarrow PA} = k_{PP}\, K_{PP-PPH}\, K_{PP}\, \mu\, P_{C_5H_{10}NH}\, C_*{}^2$$

$$\delta = 1 + K_P\, P_{C_5H_5N} + K_{PP} P_{C_5H_{10}NH} + K_{NH_3} P_{NH_3}$$

$$\mu = K_{H_2} P_{H_2} + K_{H_2S} P_{H_2S} \qquad C_* = C_{*,tot} \,/\, \left(\delta + \mu \frac{C_{S^{2-}}}{C_{S^{2-}H^+}} \right)$$

[b]C.M.C. Romero, J.W. Thybaut, G.B. Marin, Catalysis Today 130 (2008) 231-242.

[b] CUS : Coordinatively unsaturated sites, SA : Sulphur anion sites

Extension of gas phase model

- the non ideality

$$\begin{cases} r_{P\rightarrow PP} = k_{p,+} K_{P-PH2}\, K_{H2}\, K_P\, {C_*}^2 \sqrt{\delta\, \mu} \left(f_{H_2} f_{C_5H_5N} - \dfrac{1}{K_{Equi}} \dfrac{f_{C_5H_{10}NH}}{{f_{H_2}}^2} \right) \\ r_{PP\rightarrow PA} = k_{PP}\, K_{PP-PPH}\, K_{PP}\, \mu\, f_{C_5H_{10}NH}\, {C_*}^2 \end{cases}$$

- site balances

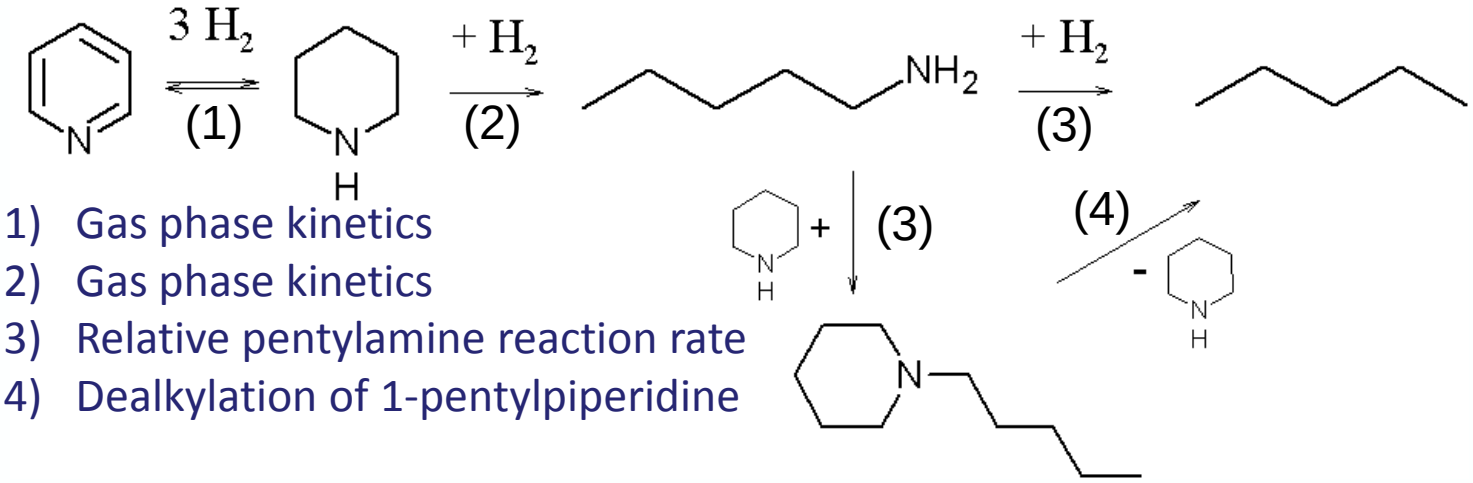
$$\begin{cases} \delta = 1 + K_P f_{C_5H_5N} + K_{PP} f_{C_5H_{10}NH} + K_{NH_3} f_{NH_3} \\ \quad + K_{solvent} f_{solvent} + K_{PentylPP} f_{PentylPP} \\ \mu = K_{H_2S}\, f_{H_2S} + K_{H_2}\, f_{H_2} \end{cases}$$

✓ Accounting for additional response,

✓ Two possible reaction networks

1. *2 Piperidine → 1-Pentylpiperidine*
2. *Piperidine + Pentylamine → 1-Pentylpiperidine*

Extension of gas phase model



1) Gas phase kinetics
2) Gas phase kinetics
3) Relative pentylamine reaction rate
4) Dealkylation of 1-pentylpiperidine

Pentyl amine denitrogenation

$$r_{PA\rightarrow C5} = k_{PA}\, K_{PA-PAH}\, K_{PA}\, \mu\, f_{C_5H_{11}NH_2}\, C_*{}^2$$

Condensation of PP and PA

$$r_{PA+PP\rightarrow PentylPP} = k_{PA+PP}\, K_{PP}\, K_{PA} \sqrt{\frac{\mu}{\delta}}\, f_{C_5H_{10}NH} f_{C_5H_{11}NH_2} C_*{}^2$$

Dealkylation of PPP

$$r_{PentylPP\rightarrow PP+C5} = k_{PentylPP}\, K_{PentylPP-PentylPPH}\, K_{PentylPP}\, \mu\, f_{PentylPP}\, C_*{}^2$$

Results : Liquid phase model

Pre exponential factors[a]

$$k = \frac{k_b T}{h} \frac{Q"_{A-H}}{Q_A Q_H} \exp - \frac{E^{o,}}{k_b T}$$

$k_{surface}$ ≈ 10^{10} to 10^{16} s^{-1} ($\Delta S \approx$ - 58 – 56 J/ mol -K)

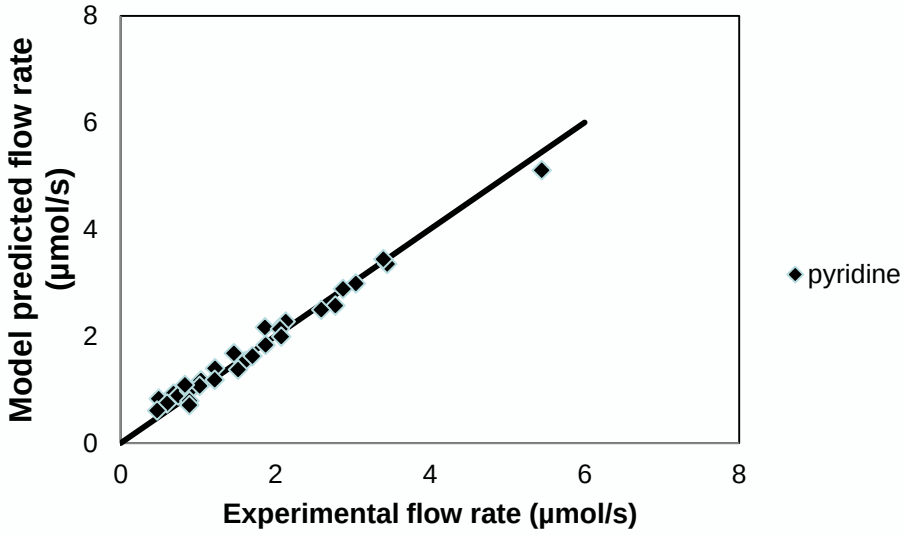
$K_{surface}$ ≈ 1 to 10^{-5}

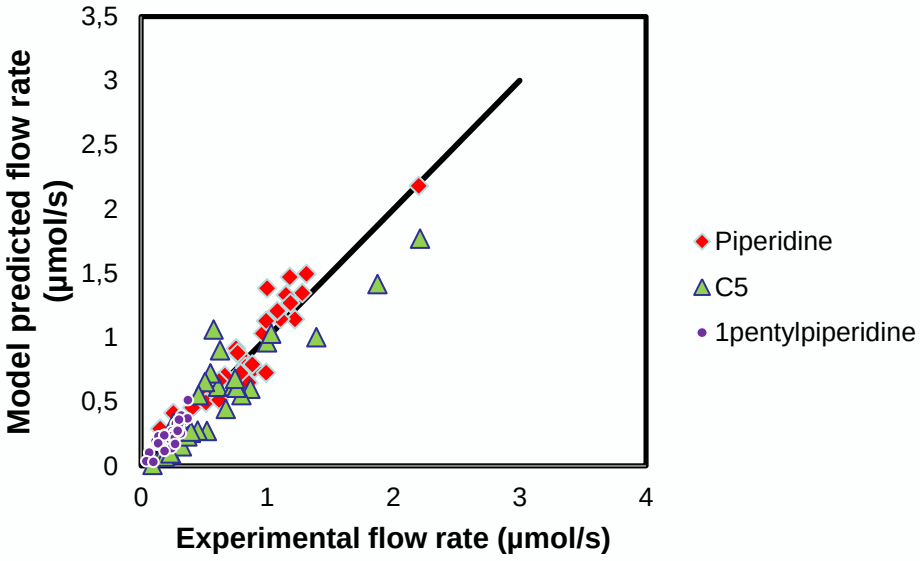
K_A ≈ 10^{-10} to 10^{-13} Pa^{-1}

$K_{H2,H2S}$ ≈ 10^{-8} to 10^{-13} Pa^{-1}

$K_{solvent}$	-ΔS	98.0	J/mol K
$K_{1\text{-pentylpiperidine}}$	-ΔS	170	J/mol K

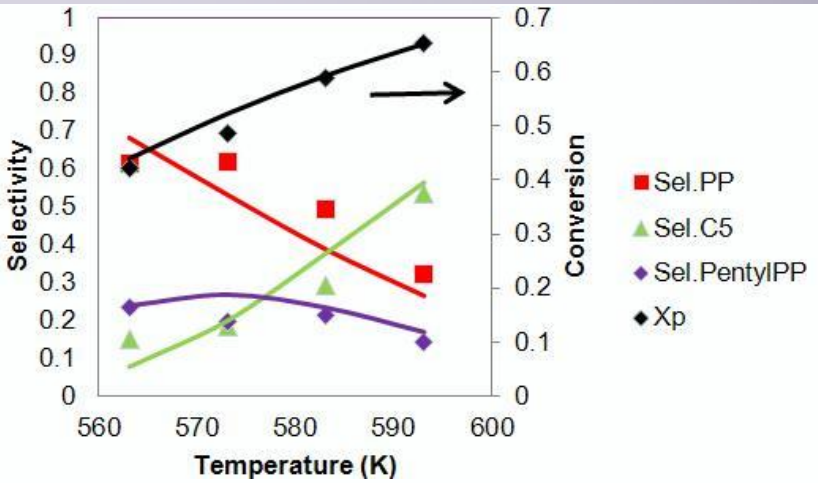
Parameter		Value	
$K_{solvent}$	-ΔH	34.5±0.77	kJ/mol
$K_{1\text{-pentylpiperidine}}$	-ΔH	85.8±1.6	kJ/mol
$k_{ratio} = \frac{k_{PA}^*}{k_{PA+PP}^*}$	E_a	108±12	kJ/mol
$k_{PentylPP->PP+C5}$	E_a	83.0± 78.0	kJ/mol
C^*	-	1.7±0.3	(-)



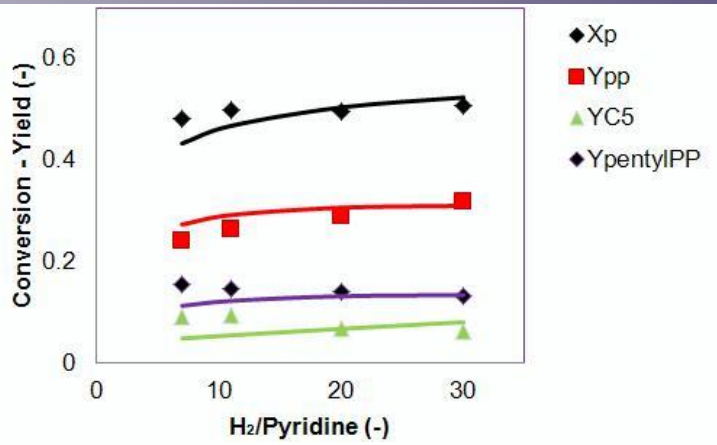


[a] J.A. Dumesic et al The Microkinetics of heterogenous catalysis, 1993

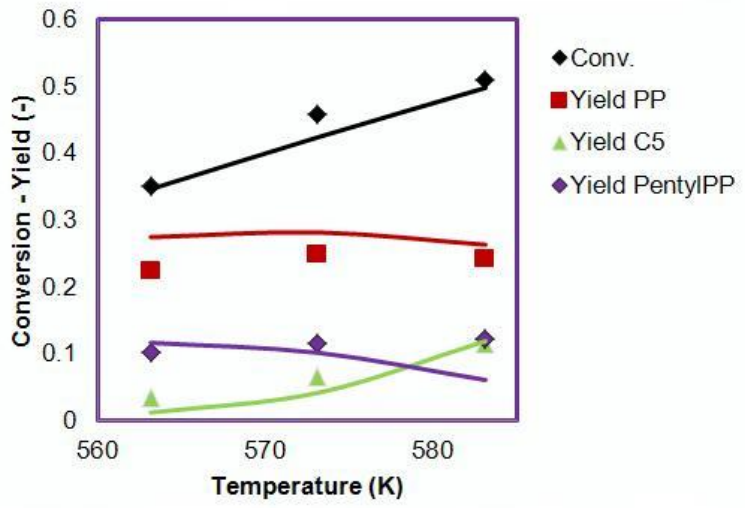
Results



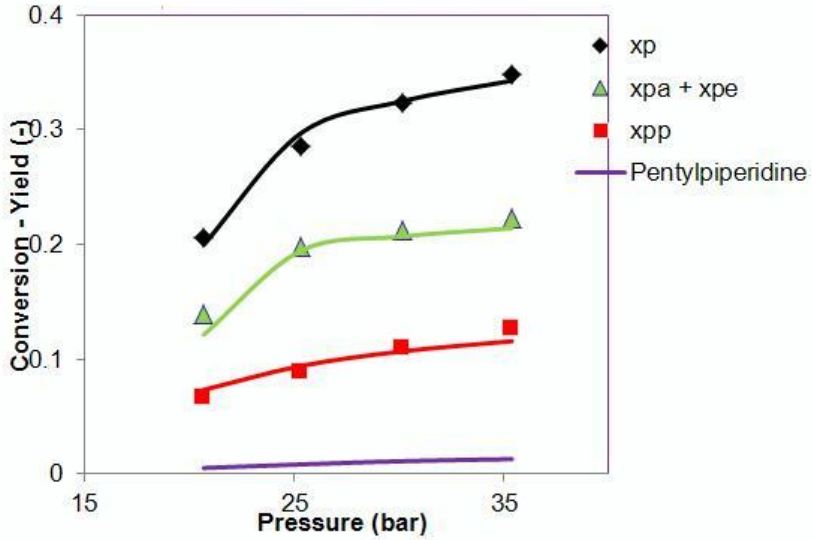
Pressure = 6.0 MPa, Space time = 790 kg s / mol, H_2/pyridine = 10, H_2S/pyridine = 0.04, Solvent/pyridine = 40;



Pressure = 6.0 MPa, Temperature = 573K, Spacetime = 564 kg.s/mol, H_2S/pyridine = 0.04; Solvent/pyridine = 40



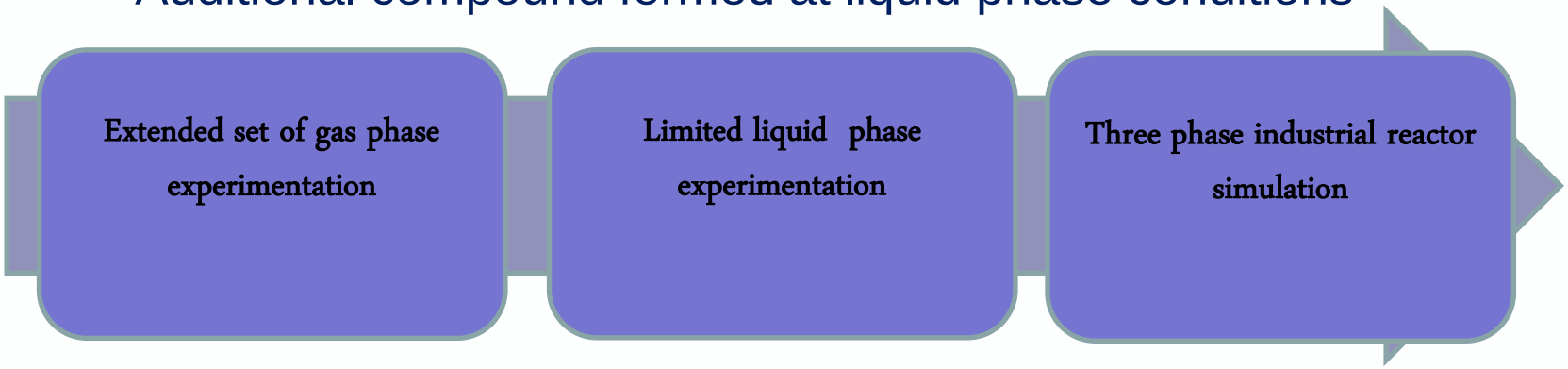
Operating conditions: total pressure = 6.0MPa, space time = 439 kg s / mol, H2/pyridine = 10, H_2S/P = 0.04, Solvent/pyridine = 40



Temperature = 573.15K, space time = 1400 kg_{cat} .s /mol, H_2/Pyridine = 620 and H_2S/Pyridine = 15, solvent/pyridine = 40

Conclusions

- Reconciliation of data at two different reaction conditions
- Effects of aggregation states (G-S / L-S) on kinetics
- Successful extension of gas phase kinetics to liquid phase reactions
  - By taking thermodynamic non ideality in liquid phase
  - Additional compound formed at liquid phase conditions



- A robust model that performed well in three phase and gas phase conditions

Acknowledgements

- The research leading to these results has received funding from the European Union Seventh Framework Programme FP7/2007-2013 under grant agreement n° 238013.

- **Dr. Haitao Huang, Dr. Steven Mitchell and Dr. John Shabaker** for sharing their technical knowhow and scientific advice during the course of this work.

Discussions

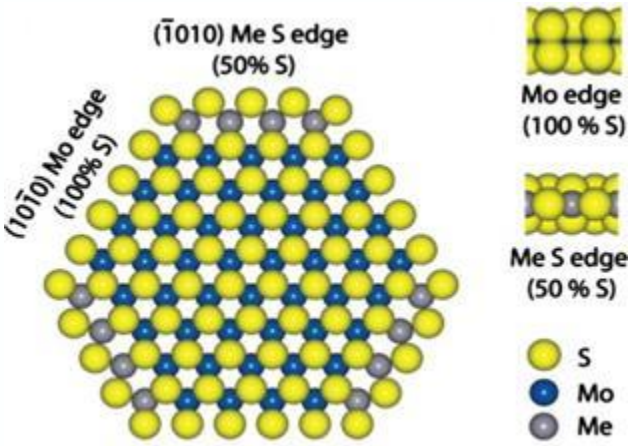
Thank you for your attention

Glossary

- *Also called active centre. Those sites for adsorption which are the effective sites for a particular heterogeneous, catalytic reaction.*
- *Aggregation State : A physically distinctive form of a substance, such as solid, liquid and gaseous state.*
- *Fugacity : Thermodynamic activity in a non ideal phase with the ideal gas state as the reference state*
- *Heterolytic dissociation :* Breaking a chemical bond to produce two oppositely charged fragments, e.g. H_2 into H^+ and H^-.

model assumptions

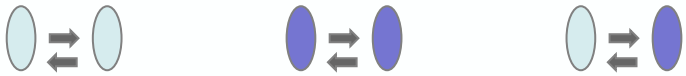
- Two sites located at the edges of the sulphided NiMo are considered.
- Hydrogenation proceeds via successive hydrogen additions either from coordinatively unsaturated sites (CUS) or from sulphur anions (SA).
- Chemisorption of hydrocarbon/nitrogen species can only occur on the coordinatively unsaturated sites due to the electronic nature of this interaction[a,b]
- No interconversion of active sites is considered because sulphydril on a CUS is electronically different from a hydrogen atom or proton on a SA



Jeppe V. Lauritsen et al, Journal of Catalysis Volume 249, Issue 2 2007 220 - 233

Thermodynamic non-ideality in the liquid phase

- ✓ Non ideality in mixtures[b]



- ✓ Chemical potential : Independent of standard state used

$$\mu_i = \mu_{i\,standard} + RT \ln a_i$$

$$\mu_i^v = \mu_i^l \qquad i = 1, \dots, n$$

- ✓ Condition for phase equilibrium

$$f_i^v = f_i^l \qquad i = 1, \dots, n$$

- ✓ Basis of V-L relationships : Relate fugacity to compositions and intensive properties (T, P)

$$f = fn(T, P, y_i)$$

[b]C.M.C. Romero, J.W. Thybaut, G.B. Marin, Catalysis Today 130 (2008) 231-242.